



Global database of surface ocean particulate organic carbon export fluxes diagnosed from the ^{234}Th technique

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Abstract. The oceanic biological carbon pump is an important factor in the global carbon cycle. Organic carbon is exported from the surface ocean mainly in the form of settling particles derived from plankton production in the upper layers of the ocean. The large variability in current estimates of the global strength of the biological carbon pump emphasises that our knowledge of a major planetary carbon flux remains poorly constrained. We present a database of 723 estimates of organic carbon export from the surface ocean derived from the ^{234}Th technique. The dataset is archived on the data repository PANGAEA[®] (www.pangea.de) under doi:10.1594/PANGAEA.809717. Data were collected from tables in papers published between 1985 and early 2013. We also present sampling dates, publication dates and sampling areas. Most of the open ocean provinces are represented by multiple measurements. However, the western Pacific, the Atlantic Arctic, South Pacific and the southern Indian Ocean are not well represented. There is a variety of integration depths ranging from surface to 300 m. Globally the fluxes ranged from 0 to 1500 mg C m⁻² d⁻¹.

1 Introduction

The concept of the biological carbon pump, dating from the late 1970s (Eppley and Peterson, 1979), quantifies the importance of oceanic primary production in the global carbon cycle. The biological carbon pump can be divided into three stages: the production of organic matter (and biominerals) in surface waters, the sinking of these particles into the deep ocean, and the subsequent decomposition of the settling (or settled) particles in the water column or the seabed. In this way the coupling of production and export processes allows the ocean to store CO₂ away from the atmosphere and contributes to the buffering of the global climate system. Without the oceanic biological carbon pump, atmospheric CO₂ concentrations would be almost twice their current levels (Sarmiento and Toggweiler, 1984). Recent studies have highlighted the challenge of quantifying the magnitude of the biological carbon pump with estimates ranging from 5 to 20 GtC yr⁻¹ (Henson et al., 2011).

There are several ways by which downward export fluxes can be estimated. We can divide the techniques into two

groups: (1) indirect estimates based on nutrient uptake (Sanders et al., 2005; Henson et al., 2006; Pondaven et al., 2000), oxygen utilization (Jenkins, 1982), radioisotopes (Buesseler et al., 1998; Cochran and Masque, 2003; Rutgers Van Der Loeff et al., 1997b; Le Moigne et al., 2012, 2013) or by synthesising numerous biological rate processes (Boyd and Newton, 1999), and (2) direct measurements from sediments traps (Lampitt et al., 2008).

Here we focus on the ^{234}Th technique, which has the advantage that its fundamental operation allows a downward flux rate to be determined from a single water column profile of thorium coupled to an estimate of the POC/ ^{234}Th ratio in sinking matter (POC is particulate organic carbon; Buesseler et al., 1992). This is highly advantageous in that it removes the complications associated with sediment trap deployments and provides an integrated estimate of export (over a timescale of weeks) rather than a snapshot of export rates (Lampitt et al., 2008).

Although several comprehensive worldwide datasets of POC flux from sediment traps have been published (e.g.

Honjo et al., 2008), to date only one thorium derived export dataset has been published (Henson et al., 2011). As part of the SeasFX project (Seasonal Variability in the Efficiency of Upper Carbon Export, <http://www.seasfx.info>, funded by the UK National Environment Research Council), we compiled a global database of ^{234}Th -derived POC export from the surface ocean (0–300 m). It comprises 723 data points from 1985 to 2013 covering most oceanic provinces. The dataset is archived on the data repository PANGAEA® (www.pangea.de) under doi:10.1594/PANGAEA.809717.

2 Data

2.1 The crux of the ^{234}Th technique

The radioactive short-lived thorium-234 (^{234}Th , $t_{1/2} = 24.1$ d) has been used as a tracer of several transport processes and particle cycling in aquatic systems by different techniques (Van der Loeff et al., 2006). The most widespread application of the ^{234}Th approach is to estimate how much POC is exported into the deep ocean (Waples et al., 2006). ^{234}Th is the daughter isotope of naturally occurring Uranium-238 (^{238}U , $t_{1/2} = 4.47 \times 10^9$ yr) that is conservative in seawater and proportional to salinity in well-oxygenated environments (Ku et al., 1977; Chen et al., 1986). Unlike ^{238}U , ^{234}Th is insoluble in seawater and is particle reactive in the water column (i.e. ^{234}Th adheres to particles as they form). As particles with ^{234}Th sink through the water column, a radioactive disequilibrium is formed between ^{238}U and ^{234}Th that can be used to quantify the rate of particle export from the surface ocean.

Export rates of ^{234}Th from the surface ocean can be calculated using a one-box model (Coale and Bruland, 1987; Buesseler et al., 1992, 1998; Cochran et al., 2000; Cochran and Masque, 2003; Savoye et al., 2006; Benitez-Nelson et al., 2001a; Verdeny et al., 2008). Assuming steady state (SS) conditions, $\frac{\partial A_2}{\partial t} = 0$ where the total ^{234}Th activity does not change with time, and no supply of ^{234}Th from physical processes (e.g. advection), the ^{234}Th flux ($\text{dpm m}^{-2} \text{d}^{-1}$), P , is calculated through the water column as

$$P = \gamma \sum_{z=0}^{z=h} (A_2 - A_1) \cdot dz. \quad (1)$$

A_1 is the total parent activity concentration (dpm m^{-3}) for ^{238}U ; A_2 is the total ^{234}Th activity concentration (dpm m^{-3}); λ is the decay constant of the daughter (d^{-1}); h is the sample depth; and P is the loss of the daughter due to sinking particles ($\text{dpm m}^{-2} \text{d}^{-1}$). In ^{234}Th studies generally advection effects are neglected, as shown in Morris et al. (2007), with the exception of upwelling regions or areas of strong advection (Murray et al., 1992; Buesseler et al., 1998). Using the SS model from a single profile of ^{234}Th activity needs to be justified as we assume that the initial activity does not change with time (Savoye et al., 2006). If several profiles of ^{234}Th activities are measured at the same site over a certain period of

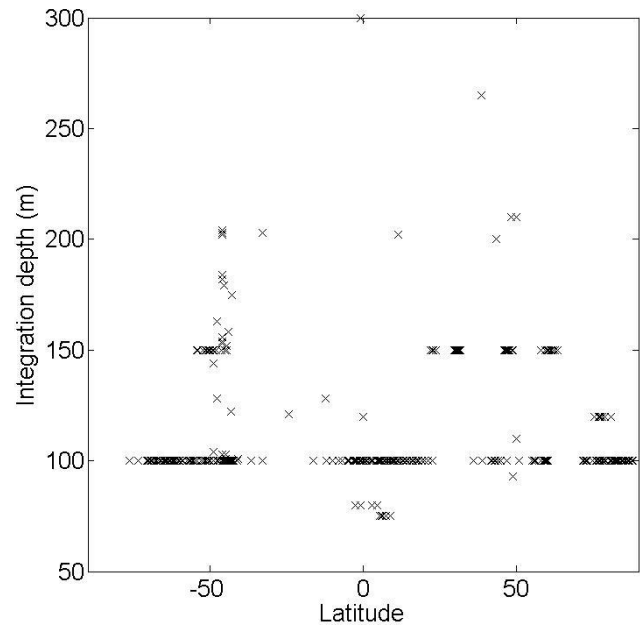


Figure 1. Integration depth of the ^{234}Th fluxes versus latitude.

time (weeks or months), a non-steady-state (NSS) model has to be applied. The NSS model may also be used during temporally variable periods with high particle flux events, such as the onset of a bloom (Buesseler et al., 1998). The NSS model factors in the term $\frac{\partial A_2}{\partial t}$ that is set to zero in the SS model (Eq. 2 below).

$$P = \lambda \sum_{z=0}^{z=h} [(A_2 - A_1)] - \frac{\partial A_2}{\partial t} dz \quad (2)$$

We report ^{234}Th fluxes from both SS and NSS models in our database. Reported ^{234}Th fluxes were integrated from depths ranging from the surface down to 300 m (Fig. 1 and Table 1). The vast majority of fluxes are integrated to between 100 and 150 m. A few studies report ^{234}Th integrated over greater depths, but not more than 300 m depth (Table 1). In the final stage of the thorium methodology, the estimated ^{234}Th flux is converted to POC export by applying the ratio of POC to particulate ^{234}Th activity.

2.2 Determination of POC : ^{234}Th ratio of sinking particles

The accuracy of the Th method relies critically on estimating the POC/ ^{234}Th ratio of material sinking from the upper ocean (Buesseler et al., 2006). This estimate is most frequently achieved by assuming that sinking carbon is contained within large particles, often greater than $50 \mu\text{m}$ in size (or $53 \mu\text{m}$, depending on the mesh supplier), whereas organic carbon within small particles is suspended in the water column, and is therefore assumed to be insufficiently large and/or dense to sink (Bishop et al., 1977; Fowler and Knauer, 1986). Size

Table 1. Sampling year, area, number of samples (N), model used (see text, Sect. 2.1), C:Th size fraction (“Part.” refers to the entire particulate fraction) and reference of studies used in the database. “Traps” is indicated when C:Th ratio were measured in sediment traps and “Equ.” refers to equilibrium depth.

Date	Area	N	Model	Integration depth (m)	C:Th ratio size fraction (μm)	Reference/investigator
1987	Equatorial Pacific	4	SS	80	Traps	Murray et al. (1989)
1992	Equatorial Pacific	65	SS	100	> 53	Buesseler et al. (1995)
1992	Equatorial Pacific	24	SS	100	> 53	Murray et al. (1996)
1992	Southern Ocean	1	SS	100	Part.	Shimmield and Ritchie (1995)
1992	Equatorial Pacific	2	SS	120	> 53	Bacon et al. (1996)
1992	Southern Ocean	10	NSS	100	Part.	Rutgers van der Loeff et al. (1997a)
1992	Equatorial Pacific	16	SS	100	> 53	Buesseler (1998)
1993–1994	Middle Atlantic Bight	7	SS	200	Traps	Santschi et al. (1999)
1995	Arabian Sea	56	NSS	100	> 53	Buesseler et al. (1998)
1996	Equatorial Atlantic	12	NSS	100	> 53	Charette and Moran (1999)
1996	Subarctic Pacific	3	SS	110–210	> 53	Charette et al. (1999)
1996	Southern Ocean	6	NSS	100	Part.	Friedrich and van der Loeff (2002)
1997	Gulf of Maine	7	SS	150	> 53	Charette et al. (2001)
1997	Southern Ocean	25	NSS/SS	100	> 70	Cochran et al. (2000)
1997	China Sea	1	SS	100	Part.	Cai et al. (2001)
1997–1998	Southern Ocean	41	NSS/SS	100	> 70	Buesseler et al. (2001)
1997–1998	Southern Ocean	28	NSS	100	> 70	Buesseler et al. (2003)
1998–1999	Arctic	15	SS	100	> 70	Amiel et al. (2002)
1999	North Pacific	4	SS	100	Part.	Chen et al. (2003)
1999	Southern Ocean	8	SS	100	> 60	Coppola et al. (2005)
1999	Labrador Sea	3	SS	100	> 53	Moran et al. (2003)
2003	North Pacific	22	SS	100	Part.	Kawakami et al. (2007)
2003–2005	Arctic	8	SS	60–120	> 53	Lalande et al. (2008)
2003	Antarctic	6	NSS/SS	100	> 70	Rodriguez y Baena et al. (2008)
2004	Arctic	8	SS	100	> 53	Lalande et al. (2007)
2004	Atlantic gyres	10	SS	Equ. depth	> 53	Thomalla et al. (2008)
2004	China Sea	36	SS	100	> 1	Cai et al. (2008)
2004	Mediterranean Sea	4	SS	200	> 70	Stewart et al. (2007)
2004–2005	Southern Ocean	20	SS	Equ. depth	> 53	Morris et al. (2007)
2004–2005	Atlantic	64	SS	150	> 53	Buesseler et al. (2008a)
2004–2005	Pacific	45	SS	150	> 53	Buesseler et al. (2009)
2005	Southern Ocean	5	SS	100	< 210	Savoye et al. (2008)
2007	Arctic	36	SS	100	Part.	Cai et al. (2010)
2007	North Atlantic	10	SS	Euphotic zone depth	> 53	Sanders et al. (2010)
2007	Southern Ocean	14	NSS/SS	60–120	> 54	Jacquet et al. (2011)
2008	Southern Ocean	27	SS	100	> 50	Rutgers van der Loeff et al. (2011)
2008	South-west Pacific	25	SS	100	Part.	Zhou et al. (2012)
2008	Southern Ocean	11	SS	100	> 53	Planchon et al. (2013)
2009	PAP site	10	SS	150	> 53	Le Moigne et al. (2013)
2010	North Atlantic	20	SS	150	> 53	Le Moigne et al. (2012)

fractions for the $\text{POC}/^{234}\text{Th}$ ratios used in the database are given in Table 1.

There is a considerable body of literature on how and why $\text{POC}/^{234}\text{Th}$ ratios vary with particle size and depth (see review in Buesseler et al., 2006); however, there is little consensus on the most appropriate ratio to use. Numerous processes can impact $\text{POC}/^{234}\text{Th}$ ratios in the ocean including particle surface-area-to-volume ratios (Santschi et al., 2006), solution chemistry issues (Guo et al., 2002; Hung et al.,

2004), the chemical composition of particles and their affinity for ^{234}Th (Szlosek et al., 2009), POC assimilation by food webs (Buesseler and Boyd, 2009), particle aggregation (Burd et al., 2000) and fragmentation (Maiti et al., 2010) and Th decay (Cai et al., 2006).

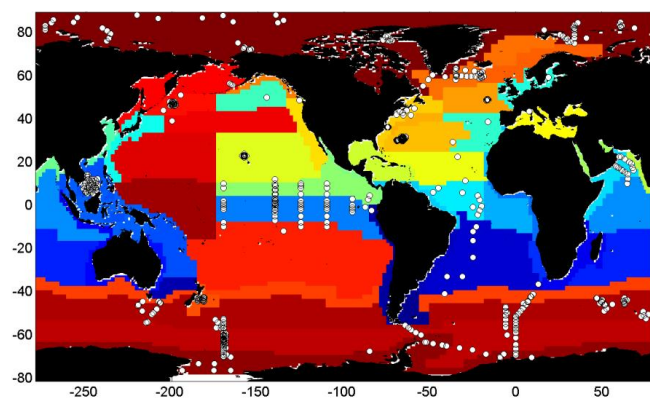


Figure 2. Map showing the distribution of sampling stations. Longhurst oceanic (Longhurst, 2006) provinces are represented in different colours.

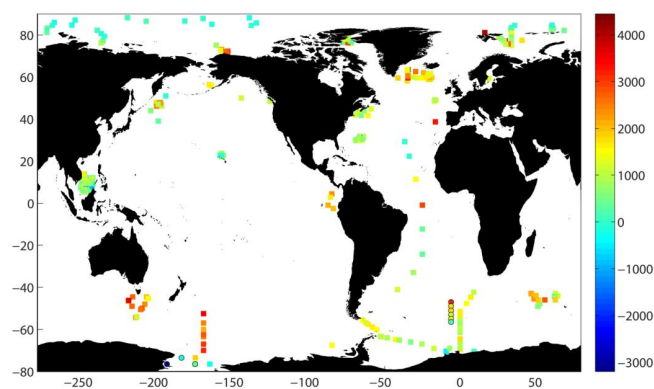


Figure 3. Global distribution of ^{234}Th export fluxes (in $\text{dpm m}^{-2} \text{d}^{-1}$). SS model (see text) derived fluxes are squares and NSS model derived fluxes are circles.

3 Results and discussion

3.1 Data sources

The dataset is archived on the data repository PANGAEA® (www.pangaea.de) under doi:10.1594/PANGAEA.809717. Latitude, longitude, date, POC flux, primary production (when available), integration depth and references are given as metadata. All fluxes were converted to $\text{mgC m}^{-2} \text{d}^{-1}$ if not already reported in these units. Th-derived POC export has been reported at 723 stations globally (Fig. 2). Some stations were part of transect cruises whereas others were part of small-scale surveys or reoccupation at different seasons and years. Sampling date, sampling area and reference investigator are given in Table 1 in addition to the literature reference. The ^{234}Th fluxes derived from both SS and NSS model are presented in Fig. 3. Because of the uncertainties associated with POC/ ^{234}Th ratios, examining the Th fluxes prior to conversion to POC fluxes provides a robust picture of the variability in particle flux on the global scale. The lowest and highest ^{234}Th flux are both measured in the Arctic Ocean.

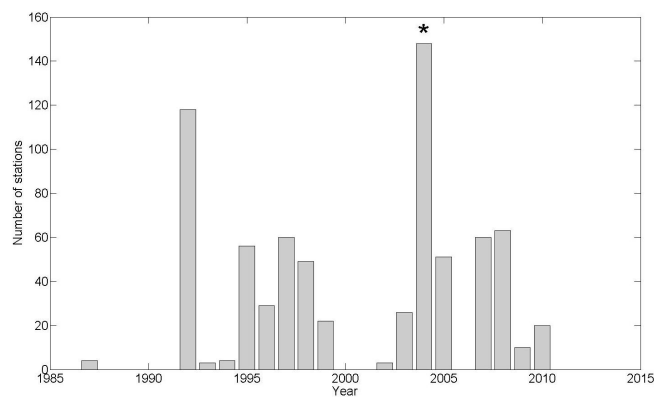


Figure 4. Histogram of datapoints presented in Table 1 and published since 1987. The star indicates the year 2004 when the VER-TIGO study was undertaken.

Also, it is worth mentioning that on small scales the ^{234}Th flux can be quite variable, e.g. in the Iceland and Irminger basins (Fig. 3). Generally, the patchiness of export, which can affect the robustness of point observations, is greater in region of high eddy kinetic energy (Resplandy et al., 2012).

Our database covers measurements published between 1985 and 2013. We do not include unpublished data here and therefore assume that the originating authors and editors have undertaken steps necessary to control data quality. Fig. 4 shows the number of thorium-derived export data per year published from 1985 to 2013. In years 1992, 1998 and 2002, the number of ^{234}Th measurements increased. This is likely due to significant improvements in the ^{234}Th methodology such as the introduction of the small volume technique (Benitez-Nelson et al., 2001b), and it also highlights dedicated carbon export programmes such as the VERTIGO voyages in the Pacific Ocean (Buesseler et al., 2008b, 2009). It is important to mention that our database only references papers where Th-derived export data are presented in tables, rather than only graphically.

More POC fluxes are reported in the Northern Hemisphere (~60 % of the database) than in the Southern Hemisphere (Fig. 5). In the Northern Hemisphere, each month of the year has been sampled (Fig. 5). Springtime (May) and summertime have been most frequently sampled. In the Southern Hemisphere, although stations are more evenly distributed in time, no ^{234}Th -derived POC export numbers are reported for winter months (July and August, Fig. 5).

3.2 Global POC export and ocean provinces

^{234}Th -derived POC export estimates are reported in 32 out of 56 Longhurst provinces (Longhurst, 2006) that are based on the prevailing role of physical forcing as a regulator of phytoplankton distribution, with measurements in most of the large open ocean biomes (Fig. 2). Figure 6 shows the mean ^{234}Th -derived POC export ($\text{mg m}^{-2} \text{d}^{-1}$) in each

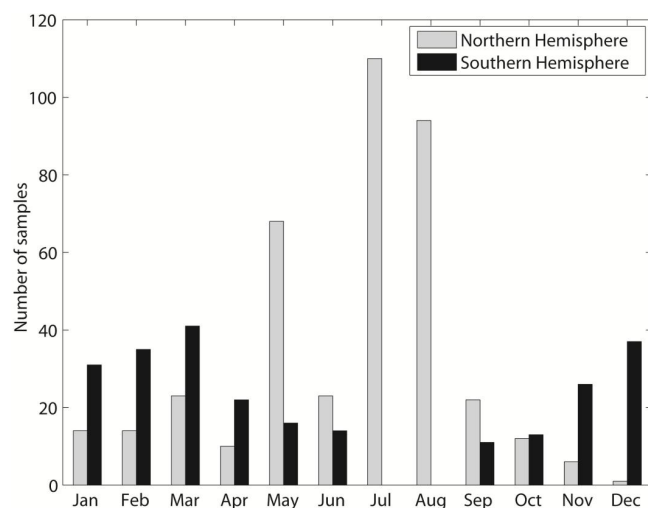


Figure 5. Number of samples collected in each month, separated into Northern Hemisphere and Southern Hemisphere.

Longhurst province that has been sampled at least once. Only four provinces are represented with one measurement (NASE, CCAL, CHIL and NECS; see Table 2 for details and provinces names).

Our dataset exhibits similar global patterns of POC export as those estimated with other methods (e.g. Laws et al., 2000; Schlitzer, 2004), with highest daily POC export rate occurring in the high-latitude North Atlantic, the Arctic and the Southern Ocean. NASE and WTRA provinces located in the subtropical and equatorial Atlantic (Fig. 6 and Table 2) are exceptions to this trend with POC export of 450 (but note that $n = 1$) and $250 \pm 200 \text{ mg m}^{-2} \text{ d}^{-1}$ reported in Thomalla et al. (2008) and Charette and Moran (1999), respectively. Some regions are relatively well sampled, such as the Arctic Ocean (Longhurst's BPLR), which is represented by 72 stations which display high spatial variability. For instance, POC flux associated with Arctic shelf regions is large while the POC flux in the central Arctic is very low (Cai et al., 2010). This implies that the magnitude of export is not necessarily a simple function of temperature in high-latitude regions.

Some regions show unexpectedly high POC flux, such as the NASE, where Thomalla et al. (2008) suggest that the occurrence of a short-lived bloom triggered by nutrient injection into the surface from a local upwelling event resulted in very high POC flux (however, note that $n = 1$ in this region). Alternatively, Charette and Moran (1999) propose that scavenging of ^{234}Th by inorganic particles may have overestimated the POC flux in the WTRA region, as also observed by Le Moigne et al. (2013); Brew et al. (2009).

A comparison of Th-derived export with direct measurements of surface export (from free drifting sediment traps to avoid any problem due to overcollection of horizontally advected material) would be useful at this stage. However,

surface POC fluxes from direct measurements are scarce. The few studies that have examined the discrepancy between ^{234}Th -derived estimates and direct measurements of POC export (e.g. Le Moigne et al., 2013; Stewart et al., 2007) suggest that ^{234}Th -derived estimates in most cases overestimate the direct POC flux. This may be due to a mismatch in timescales over which different methods estimate export. ^{234}Th deficits persist after an export event, whereas free-drifting sediment traps capture only the instantaneous export flux.

3.3 Towards better understanding of the ocean's biological carbon pump

A portion of this database has already been used to extrapolate the local measurements to a global scale by correlation with satellite sea surface temperature fields (Henson et al., 2011). The resulting estimates of global integrated carbon export were significantly lower than those derived from new production measurements, at just $\sim 5 \text{ GtC yr}^{-1}$ compared to 12 GtC yr^{-1} (Laws et al., 2000). However, the parameterisation of the export ratio presented in Henson et al. (2011) has relatively large uncertainty at cold sea surface temperature (SST) (see their Fig. 2). As the type of phytoplankton present in the upper ocean may also influence the export ratio (because large, dense phytoplankton cells sink rapidly and export more efficiently than smaller plankton), the variability in export ratio at low temperatures could be due to large seasonal shifts in phytoplankton community structure at high latitudes.

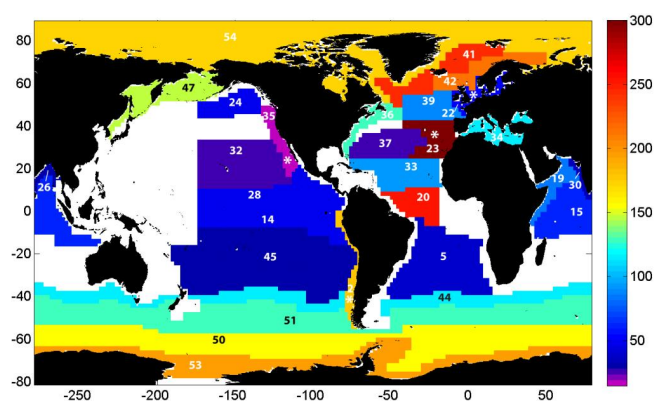
In high-latitude regions, simultaneous measurements of upper ocean particulate organic carbon flux and phytoplankton community structure could help to assess how seasonal variability of the phytoplankton bloom alters the export ratio. The knowledge gained from this approach could then be applied to our global dataset, combining satellite-derived data on SST, bloom stage and phytoplankton community structure. Ultimately, a revised parameterisation of the export ratio, including relevant seasonal information, could be used to calculate a new global estimate of the magnitude of the biological carbon pump.

3.4 Significant gaps in the global dataset

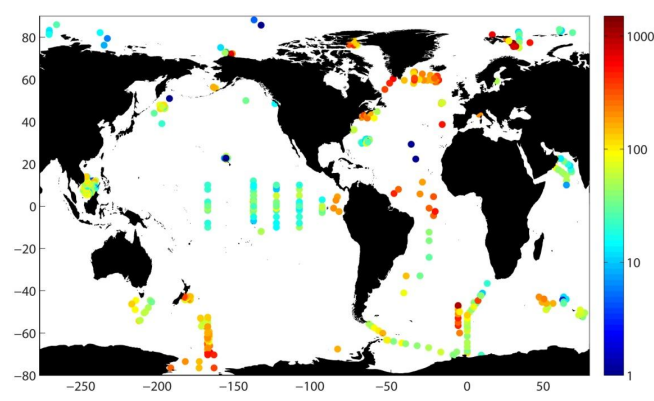
Globally the Th-derived POC fluxes ranged from 0 to $1500 \text{ mg of C m}^{-2} \text{ d}^{-1}$ (Fig. 7). In this database, some areas such as the equatorial Pacific, Arabian Sea, South China Sea and the high-latitude North Atlantic are fairly well represented (Fig. 7). However, there are significant gaps that could potentially bias estimates of the global carbon export. Most notably, ^{234}Th -derived POC fluxes are not reported for the Benguela system (BENG), the Mauritanian upwelling (CNRY; ETRA), the entire western Pacific (consisting of numerous Longhurst provinces), and the southern Indian Ocean (ISSG).

Table 2. Mean POC flux ($\text{mg m}^{-2} \text{d}^{-1}$) per Longhurst province (Longhurst, 2006).

Province number	Province name	Mean POC flux ($\text{mgC m}^{-2} \text{d}^{-1}$)	Standard deviation in POC flux	Number of stations
2	CHIL – Chile-Peru Current Coastal	176.00	0	1
5	SATL – South Atlantic Gyre	37.44	54.38	7
14	PEQD – Pacific Equatorial Divergence	46.20	40.43	71
15	MONS – Indian Monsoon Gyre	62.16	54.26	10
19	ARAB – NW Arabian Upwelling	85.18	82.45	48
20	WTRA – Western Tropical Atlantic	251.39	178.19	10
22	NECS – NE Atlantic Shelves	53.52	0	1
23	NASE – North Atlantic Subtropical Gyre (East)	488.40	0	1
24	PSAE – Pacific Subarctic Gyre (East)	49.00	32.39	6
26	INDE – East India Coastal	31.60	15.66	3
28	PNEC – North Pacific Equatorial Countercurrent	48.65	50.29	24
30	INDW – West India Coastal	33.60	52.43	18
32	NPTG – North Pacific Tropical Gyre	26.27	23.57	21
33	NATR – North Atlantic Tropical Gyre	91.20	128.98	2
34	MEDI – Mediterranean Sea, Black Sea	115.80	78.70	4
35	CCAL – California Upwelling Coastal	14.76	0	1
36	NWCS – NW Atlantic Shelves	127.08	97.75	14
37	NASW – North Atlantic Subtropical Gyre (West)	25.90	19.41	65
39	NADR – North Atlantic Drift	87.56	51.22	11
41	ARCT – Atlantic Arctic	242.34	122.65	16
42	SARC – Atlantic Subarctic	214.67	127.06	14
44	SSTC – South Subtropical Convergence	114.34	136.16	7
45	SPSG – South Pacific Subtropical Gyre	28.79	13.73	10
47	BERS – North Pacific Epicontinental	146.00	24.04	3
50	ANTA – Antarctic	156.95	100.90	67
51	SANT – Subantarctic	126.54	116.71	107
53	APLR – Austral Polar	195.07	233.32	41
54	BPLR – Boreal Polar	171.05	298.48	72

**Figure 6.** Mean POC export ($\text{mg m}^{-2} \text{d}^{-1}$) in Longhurst provinces (provinces with only one measurement are marked with a star). Areas in white represent areas where no data have been collected. Numbers on map indicate Longhurst province (cf. Table 2).

Some of these areas are deemed to be high production and export regions due to the occurrence of upwelling. For example, deep (~ 2000 m) sediment trap measurements of POC

**Figure 7.** Global distribution of POC export fluxes derived from the ^{234}Th technique (in $\text{mg m}^{-2} \text{d}^{-1}$).

export for the Mauritanian upwelling suggest that POC flux can peak at 5 to $25 \text{ mg m}^{-2} \text{d}^{-1}$ (Fischer et al., 2009), and is therefore presumably higher in the upper water column. Also, in the Benguela system POC export has been estimated to be $550 \text{ mg m}^{-2} \text{d}^{-1}$ on the basis of nutrient uptake (Waldrón et al., 1992). Provinces such as KURO and PSAW in

the north-west Pacific may also export a significant amount of POC ($\sim 120 \text{ mg m}^{-2} \text{ d}^{-1}$ averaged over one year based on a modelling study (Schlitzer, 2004). Although these regions represent a small percentage of the global surface area of the ocean, the lack of data in these high export areas could potentially result in estimates of global POC export that are biased low.

We suggest that future studies should investigate ^{234}Th -derived POC export flux in regions that are currently unsampled or undersampled. However, in upwelling regions where advective current velocities are high, the influence of advection and diffusion on the ^{234}Th model should be carefully assessed and accounted for in the calculation of POC flux, as done, for example, in Morris et al. (2007), Buesseler et al. (1998), and Charette et al. (1999).

4 Conclusions

Here we provide a global database of 723 published estimates of POC export derived from the ^{234}Th technique spanning 1985–2013. The observed pattern of POC fluxes reflects the expected dynamics of primary production and export. Some notable gaps in the dataset are the Benguela system, the Mauritanian upwelling, the western Pacific, and the southern Indian Ocean. This database could be used to provide revised and more robust estimates of the ocean's biological carbon pump.

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